

# Introducing Cerium Based High Energy Redox Batteries

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## Introduction

Consideration of the table of electrode potentials indicates that cerium ion could be a candidate for a high energy positive electrolyte in a redox battery. However, two issues have limited its use in practical devices. These are its low solubility in aqueous solution and the need for a compatible high-energy negative electrolyte. The identification of methanesulfonic acid (MSA) as the best electrolyte for cerium is due to Kreh et al <sup>(1)</sup>, the application of this to a electric storage batteries is novel. In this later respect examples of potential couples include zinc/cerium, chromium<sup>+2</sup>/cerium, vanadium<sup>+2</sup>/cerium and titanium<sup>+3</sup>/cerium. These and others using alternative negative electrode candidates, can be used in batteries using cerium with or without MSA as the common electrolyte.

Several options for a negative redox couple compatible with cerium/MSA were studied in the laboratory. Some of us had worked on a cerium<sup>+4</sup>/titanium<sup>+3</sup> system where the cerium<sup>+4</sup> side of the redox was used to oxidize aromatic carbonyl groups and titanium<sup>+3</sup> was used to reduce nitro compounds. This work which had been pursued for many years, gave us invaluable experience with the cerium redox system in terms of flow cell design and materials of construction as well as the characterization of the electrode processes. Our aim has always been to convert this most useful reagent into practical use <sup>(2,3,4)</sup> and we have operated the system at large pilot plant and commercial scale <sup>(5,6,7)</sup> in one form or another over the years as a means to manufacture high yield, high purity organic chemicals. It is perhaps for this reason alone we were not restrained in our thinking that a redox battery using this part as a couple was a practical, efficient and useful possibility.

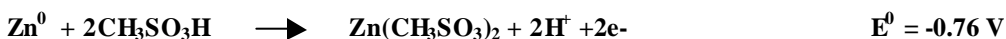
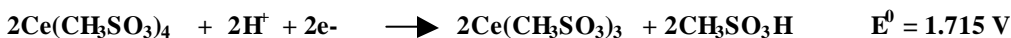
The following conditions will maximize a flow battery's market appeal:

- Installed capital costs which are competitive with the established competition (simple cycle gas turbines and valve regulated lead acid batteries);
- 'instant-on' capability, long life and repeatable performance;
- minimum maintenance and pre-fabricated modular construction;
- minimal environmental impact.

## System chemistry

For our first commercial system, the positive ceric/cerous ion couple is used in combination with zinc<sup>0</sup>/zinc<sup>+2</sup> ion. Early experiments gave an open circuit voltage of 2.43 V. The Ce<sup>+4</sup> electrode in the charging mode of the battery is operating at a minimum of +1.7 volts vs NHE<sup>(8)</sup>. Note that thermodynamic potential for water electrolysis is 1.23 volts so water electrolysis is thermodynamically favored. The high oxygen and hydrogen overpotentials, however, reduce the rates of these parasitic reactions significantly. In our case the oxidation of Ce<sup>+3</sup> to Ce<sup>+4</sup> and the reduction of Zn<sup>+2</sup> to Zn<sup>0</sup> are kinetically favored and proceed at high current efficiencies.

The main electrode reactions (written as discharges) are:



A simple laboratory scale flow cell with a Nafion membrane and platinized titanium and carbon electrodes was constructed and gave an open circuit voltage of 2.43 volts at room temperature. This simple parallel plate reactor lab cell was actually charged and discharged many times and gave very repeatable results. At room temperature and wide inter-electrode and separator gaps of 1cm, the parasitic losses due to the high internal resistance (IR) affected the round trip efficiency (energy in/energy out). However, the cell had high coulombic

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efficiency at both the positive and negative electrodes. It was also noted that the parasitic losses due to corrosion of the deposited zinc in MSA at the top of charge was much less than with other electrolytes. We concluded the electrochemical redox system had merit as a battery and that optimal cell design and system engineering would yield a very competitive battery.

### Electrolytes

Zinc methanesulfonate and cerium methanesulfonate had sufficient solubility, see Table 1 to adapt the battery couple to a common electrolyte.

Table 1. Solubility of selected metal methanesulfonates compared to their sulfates and chlorides.<sup>(9)</sup>

Metal Cation	CH <sub>3</sub> SO <sub>3</sub> H	H <sub>2</sub> SO <sub>4</sub>	HCl
Ag	2.60	0.055	0
Hg	1.81	0	0.24
Pb	2.6	0	0.034
Zn	2.16	3.32	13.0
Mn	2.9	3.52	4.12

Figures in columns are given in mol dm<sup>-3</sup> as the metal

Although zinc is more soluble in sulfuric and hydrochloric acid, MSA is favored as zinc dendrites do not form as easily during plating (i.e. charging) and zinc is sufficiently soluble to avoid mass transport problems at the top of charge. Hydrochloric acid is unacceptable as even with an ionic exchange membrane in place, chloride ions pass to some extent causing problems with chlorine gas generation at the anode. This would negate our philosophy concerning the development of an environmentally friendly battery. The question becomes, what penalty in terms of IR drop would be suffered in bipolar battery configuration with a 2-3 mm cell gap by using MSA. Calculations show that this would amount at most to several millivolts, an acceptable penalty when weighed with the benefits.

Table 2. The equivalent conductance of aqueous solutions of MSA and other common acids in S cm<sup>2</sup> mol<sup>-1</sup>

Acid	2N	1N	0.5N	0.1N	0.05N	0.01N
HCl	-	341.11	373.53	403.63	412.12	421.8
H <sub>2</sub> SO <sub>4</sub>	413.84	444.88	464.12	529.08	572.76	699.40
CH <sub>3</sub> SO <sub>3</sub> H (MSA)	232.97	299.6	336.47	372.72	381.76	391.78

One common problem with redox systems is the mixing of the two electrolytes over time. This happens even when ion exchange membranes are used. This can cause a decline in performance that must be remedied by periodic electrolyte treatment. A key feature of this system is the opportunity to use a common "mixed electrolyte" from the start. Both positive and negative electrolytes contain Ce and Zn in similar amounts. This is a situation that would occur after many cycles without electrolyte maintenance. If the battery can be made to operate in this condition then electrolyte maintenance is eliminated. Cerium cannot be electrodeposited from aqueous solution at the potential of the Zn/Zn<sup>2+</sup> couple, and Zn<sup>2+</sup> does not have additional oxidation states that interfere with the Ce<sup>3+</sup>/Ce<sup>4+</sup> couple. Therefore, the presence of cerium has little impact on the Zn/Zn<sup>2+</sup> couple and vice versa.

Electrolytes were prepared from methanesulfonic acid (MSA, 70%, Atofina Chemicals), cerium carbonate (Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>, Advanced Material Resources), zinc oxide (ZnO, Zochem) and de-ionized water. At least 90% of the de-ionized water required was added to a beaker. Then Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> was added, and slurried with the water. Next, about one-third of the MSA was added slowly, until all of the Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> had dissolved. This process was accompanied by the evolution of CO<sub>2</sub> gas. The remaining MSA was added in five or six batches, alternating with additions of ZnO. The addition of ZnO was strongly exothermic; following each addition the solution was cooled to 35 °C to 40 °C before the next addition. Finally, the volume was adjusted to the desired value by adding de-ionized water, as necessary.

### Electrode and membrane study

Previous experience with cerium ions with various electrodes and electrolytes including MSA and reference to the literature showed that high efficiencies (70-95%) during the oxidation process were possible. Obviously in

cases where diminishing concentrations of cerous ions occurred current efficiencies were lower due to mass transfer limiting conditions. The classical way to deal with this problem is to operate the system below complete conversion of cerous to ceric and/or increase the turbulence at the electrode electrolyte interface. The later strategy is paid for in increased pumping costs, which is not necessarily the best option for a battery system. Platinum coated titanium and iridium oxide coated titanium were initially our first choice as we had previously operated such electrodes at  $4000 \text{ amps/m}^2$  over many months without significant wear or loss of efficiency. Glassy carbon in the form of carbon fiber and as solid plate is now a serious candidate undergoing life testing. Coated Magneli phase titanium suboxides (Ebonex<sup>®</sup>)<sup>(9)</sup> have been used previously with success and make ideal bipoles that can be reversed in battery operations.

Nafion was initially used as the separator but this became unnecessary and has been replaced with low cost micro-porous separators. This feature has much to do with the relative transport through electrolyte and a fine porous diaphragm of solvated protons compared to complexed ceric ions which are very much larger. Note also that having both electrolytes at the same isotonic concentration eliminates osmotic effects and concentration gradients across the separator. When an ion exchange membrane was tested against a porous teflon separator it was noted that the coulombic efficiencies of the zinc electrode were almost identical but the charging voltage was lower. Apart from the relative cost of the two very different types of separator, the drop in charging voltage was acceptable in its own right.



Lab cell

Cells on test

$1 \text{ m}^2$  Pilot Cell

### **Battery Construction**

Batteries were constructed from dished-electrode membrane (DEM) cells, electrolyte reservoirs and the associated pumps and tubing used to connect the two and provide flow. The cell bodies were made from ultra-high molecular weight polyethylene, UHMWP, the reservoirs were HDPE and PDVF was used for all tubing and fittings, except for a short section in the peristaltic pump head, which was PVC. The active surface area was  $100 \text{ cm}^2$  ( $10 \text{ cm} \times 10 \text{ cm}$ ). These batteries were cycled using an 8-channel MACCOR Series 2300 tester. Typically, cells were charged at  $400 \text{ A/m}^2$  to  $500 \text{ A/m}^2$ , and discharged at  $1.8 \text{ V}$ . Other discharge voltages in the range  $1.2 \text{ V}$  to  $2.2 \text{ V}$  were also used.

A pilot battery consisting of a  $1 \text{ m}^2$  cell has been built and demonstrated. The cell body was adapted from a unit used to operate a pilot plant for the manufacture of naphthaquinone. The design is based on a dished electrode cell. This was partly for expedience but also as we had extensive operating data from this device and we could easily access the impact of the modifications in the electrolyte. The cell geometry was equivalent to that used for life testing in the laboratory study. A series of charge discharge cycles identical to the lab tests observed in the laboratory were run.

Using this pilot system and identical electrolyte compositions the performance data was very close to that found in the laboratory cells. Note that both laboratory and Pilot cell were side fed which require unnecessarily large inter cell gaps. This issue will be dealt with in our engineering program. Together with numerous laboratory and intermediate scale batteries, these non-optimized cells have been extensively cycled at power densities ranging between  $600$  and  $800 \text{ W/m}^2$ . Some additional work has been completed at  $1300 \text{ W/m}^2$ .

We are now working to explore higher power densities with more fully optimized cells. This work will more fully define the performance of both low cost and higher cost electrode and membrane materials and allow more detailed engineering trade offs to be made.

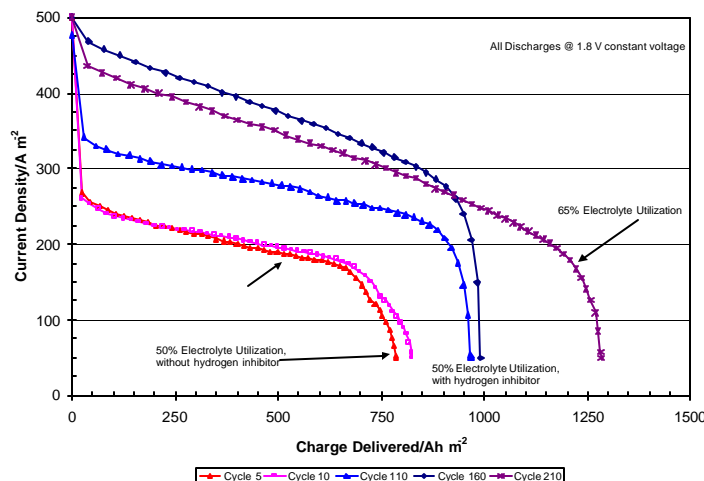


Figure 1. Typical discharge curves of Zn/Ce Redox Battery (Cell 405)

Figure 1 shows typical discharge curves of the Zn/Ce redox battery, for an un-optimized cell (Pt-Ti, Carbon electrodes, large cell gap, 1.3 cm). Cells were typically discharged at 1.8 V constant voltage, so the discharge curves are shown as current densities. The difference in behavior of the different curves is largely due to the test conditions. Typically, cells have been cycled at about 50% electrolyte utilization. At about cycle 60, a trace amount of an inhibitor for hydrogen evolution was added to the negative electrolyte, the effect of this was to increase the discharge capacity from about 800 Ah/m<sup>2</sup> to 1000 Ah/m<sup>2</sup> (for a 1200 Ah/m<sup>2</sup> charge). At cycle 186 the utilization of the electrolyte was increased to 65%, the discharge capacity was increased proportionately. Differences in the current density shown in this figure were due mostly to flow rate and temperature increases.

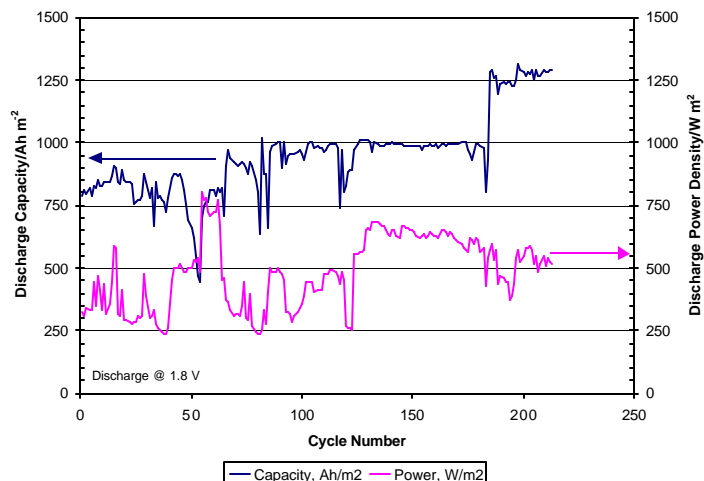


Figure 2. Effect of cycle number on discharge capacity and discharge power of Cell 405

Figure 2 shows the discharge capacity (Ah/m<sup>2</sup>) and power density (W/m<sup>2</sup>) as a function of cycle number. Essentially there is no capacity fade out to 200+ cycles. Glitches in the test hardware caused the low-capacity cycles shown in the figure. This figure shows the effect of the addition of the hydrogen inhibitor at about cycle 60, and the increase in electrolyte utilization at cycle 186. The power density (average voltage x average discharge current) is more varied, ranging from a low of 250 W/m<sup>2</sup> to a maximum of 750 W/m<sup>2</sup>. The variation in power density is due mostly to temperature and flow rate effects. It is important to note that the cell shown in

Figures 1 and 2 had a large cell gap, which increases the IR voltage loss, and therefore also reduces the average power density.

Figure 3 shows the effect of discharge voltage on the power density delivered by the battery. In this figure the power density is calculated as the discharge voltage times the current density. The maximum average discharge power, 960 W/m<sup>2</sup>, is achieved for discharge at 1.4 V. Once again, it is important to note that the cell gap for the Cell shown in Figure 3 was large, at least 1.5 cm.

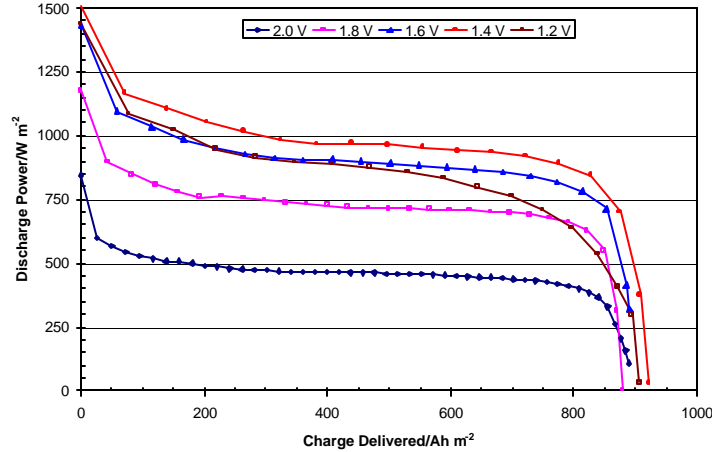


Figure 3. Effect of Discharge Voltage on Discharge power density (Cell 107)

Figure 4 shows the discharge power for a cell containing the same electrode materials as cells 405 and 107, but using a PTFE separator and having a 0.6 to 0.7 cm cell gap. Comparison of the relevant curve in Figure 3 with Figure 4 shows that the flat portion of the discharge curve is increased from about 700-750 W/m<sup>2</sup> to about 900-950 W/m<sup>2</sup> by the narrower cell gap. The average value as a function of cycle number, about 820 W/m<sup>2</sup>, is also shown in Figure 4.

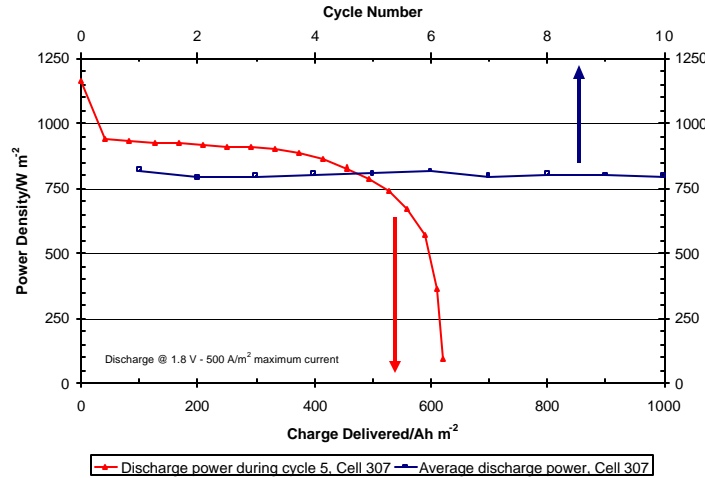


Figure 4. Discharge Power of Cell 307

### 1 m<sup>2</sup> Pilot Cell

Figure 5 shows the discharge power of the 1 m<sup>2</sup> pilot cell. The major difference between the lab cells and the Pilot Cell was that the pilot cell contained a lead negative electrode. From cycle 1 to cycle 7, this cell was discharged at 2.0 V; the average discharge power was 350 W/m<sup>2</sup>. From Cycle 8 onwards, the cell was discharged at 1.8 V, and gave 600 W/m<sup>2</sup> average discharge power.

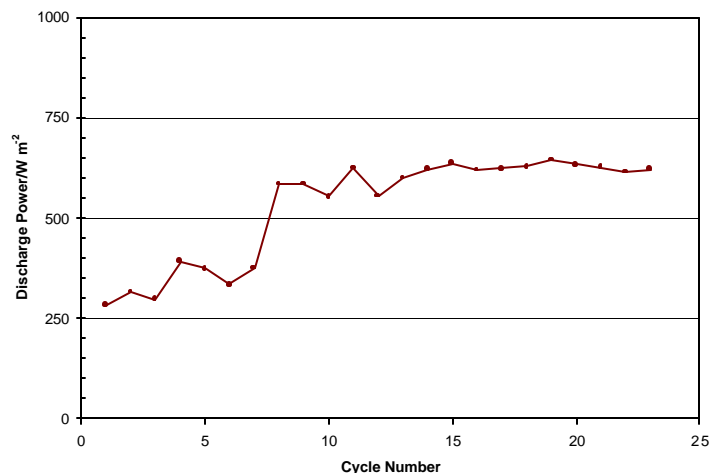


Figure 5. Discharge Power of 1 m<sup>2</sup> Pilot Cell

## Conclusions

The cerium zinc redox couple appears to hold great promise as most of the chemical and electrochemical problems can be overcome and the high voltages and high current densities can be realized in practice. The next stage is to turn this into practical high capacity storage batteries by the application of good engineering and efficient manufacturing practices. We have assembled such a team to achieve these objectives and plan to exploit the potential of this new battery concept.

## References

- [1] US patents 4,639,298; 4,670,108; 4,701,245 to Kreh et al. See also Spotnitz, et al. J. Appl. Electrochem 90 (2) 1990, p 209
- [2] Indirect electrochemical process for the production of naphthaquinone. I.M. Dalrymple and J.P. Millington. J applied Electrochemistry (1986) 885-893.
- [3] Organic electrosynthesis of aromatic aldehydes and quinones. S. Harrison, A. Théorêt et A. Velin. Chemical Specialties USA 1993. Pittsburgh, September, 1993
- [4] Titanium and cerium containing acidic electrolyte. S. Harrison. US Patent 5,679, 235, November 1997
- [5] Electrochemical redox reagents, some applications and process limitations in electrochemical synthesis. R. L. Clarke and S. Harrison. Electrochemical Society (abstract 758) San Francisco, 22-27 May 1994.
- [6] Electrosynthesis of Anthraquinone. S. Harrison and A. Théorêt. Journal of New Materials for Electrochemical Systems. Vol 1, Number 1, 1, 1999.
- [7] Electrosynthesis of aminoanthraquinone. . Fundamental and Potential Applications. S. Harrison and K. Amouzegar. Ed. Weaver, Fisher, Kahlhammer and Mazur. Electrochemical Society Proceedings, 1997
- [8] Atlas of Electrochemical Equilibria in aqueous solutions. Marcel Pourbaix. NACE 1974
- [9] Environmental benefits of methanesulfonic acid. M.D. Gernon, M. Wu, T. Buszta and P. Janney. Green Chemistry. June 1999. RSC publication UK.
- [10] Electrodes based on Magneli phase titanium oxides, a review of the properties and applications of Ebonex®. James R. Smith, Robert L. Clarke and Frank C. Walsh. Journal of Applied Electrochemistry 1997.